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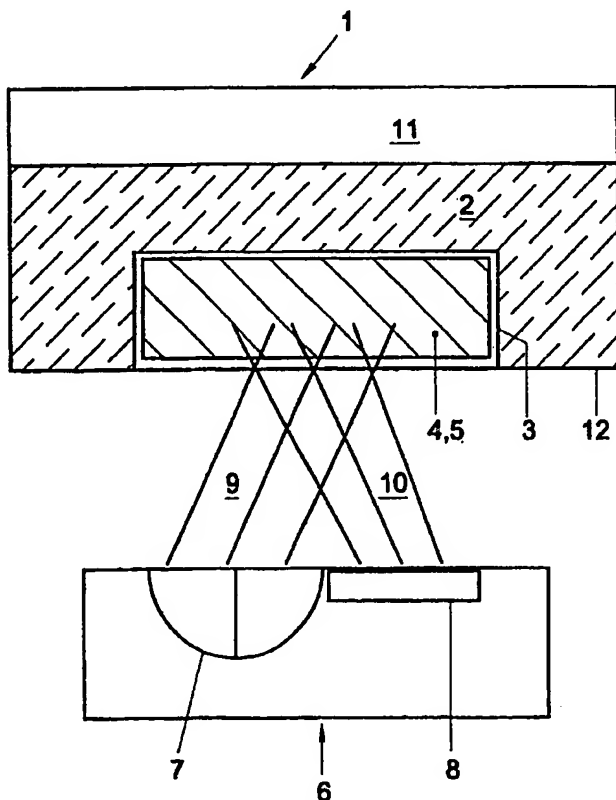
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- (72) Inventor; and  
(75) Inventor/Applicant (for US only): **DRAAIJER, Arie** [NL/NL]; Nijenheim 6314, NL-3704 BM Zeist (NL).
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- (74) Agent: **PRINS, A., W.**; Vereenigde, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).
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- (71) Applicant (for all designated States except US): **NED-ERLANDSE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOEK TNO** [NL/NL]; Schoemakerstraat 97, NL-2628 VK Delft (NL).
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(54) Title: OPTICAL SENSOR FOR MEASURING OXYGEN



(57) Abstract: The invention has for its object to provide a substrate for embedding oxygen sensitive dye, while the thus formed sensor is chemically stable to a high degree, has a high temperature resistance in the relevant temperature range, and is gas permeable to a high extent. This object is achieved in that the substrate consists of a fluorinated silicone polymer. The invention can be applied with particular advantage if the medium is a consumable oil, such as, for instance, sunflower oil, or if a measurement is performed at relatively high temperatures or in chemically aggressive environments. An additional advantageous property is that the substrate is found to adhere well to glass. As a consequence, in practice, the oxygen content can be simply determined in consumable oil products stored in glass, from which in turn a storage life can be derived, and the sensor will not come loose at high temperatures or in chemically aggressive environments.

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IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

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- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

Title: Optical sensor for measuring oxygen

This invention relates to an optical sensor for measuring oxygen in a medium, provided with a substrate in which an organometallic complex is embedded.

The organometallic complex is an oxygen-sensitive  
5 fluorescent dye, with the amount of fluorescence and the fluorescence life being dependent on the oxygen content in the medium. Such an organometal typically consists of Tris-Ru<sup>2+</sup>-4,7-biphenyl-1,10-phenanthroline; this  
Ru(ruthenium) complex is particularly oxygen-sensitive, but  
10 other organometals can also be used, such as an Os complex or a Pt complex.

The organometallic complex is normally adsorbed to a silica gel. The silica gel can adsorb a high concentration of the dye without the fluorescent properties of the  
15 material being thereby affected. The silica gel with the adsorbed dye is embedded in a substrate of polymeric material, for instance a mixture of PDMS (polydimethylsiloxane) and PTMSP (polytrimethylsilylpropyl), which polymers are gas permeable to a high degree, so that the  
20 response of the sensor to oxygen content changes can be prompt. By being embedded in the substrate, the organometallic complex is rendered insensitive to disturbing influences, such as, for instance, the action of moisture or leaching of the fluorescent component.

25 Through fluorescence measurements, the level of the oxygen content in the medium can be determined. Such a measurement is relatively simple to carry out, but has as a disadvantage that the measuring results, owing to the occurrence of, for instance, photobleaching or ageing of  
30 the sensor due to high temperatures, are no longer reproducible with the passage of time.

This phenomenon occurs in particular if measurements are performed where the medium consists of consumable oil,

such as fish oil, sunflower oil, etc. In practice, there is an interest in determining the oxygen content in such media for the purpose of assessing the storage life thereof.

Through chemical action of the medium, however,

5 measurements with the sensor applied heretofore have been found to become unreliable with the passage of time.

This phenomenon also occurs as a result of a high temperature loading of the sensor, for instance when using the sensor as a feedback for the gas-air ratio in  
10 combustion apparatus. Further, this phenomenon occurs if the sensor is exposed for a relatively long time, for instance in the case of oxygen content measurements in groundwater.

It is attempted to obviate these problems by  
15 stabilizing the sensor. This has shown that an inherently chemically stable and gas permeable substrate material is not straightforwardly satisfactory: for that, the chemical interaction with the embedded dye, which must retain its oxygen-sensitive properties, and the substrate is too  
20 complex. To date, therefore, there is not any substrate known which, in combination with the oxygen-sensitive dye, continues to retain its favorable properties.

Accordingly, the object of the invention is to solve the above-described problem and to provide a substrate for  
25 embedding oxygen-sensitive dye, while the thus formed sensor is chemically stable to a high degree, has a high temperature resistance in the relevant temperature range, and is gas permeable to a high extent.

This object is achieved in that the substrate  
30 consists of a fluoridated silicone polymer. Surprisingly, it was found from experiments that such a polymer possesses the required properties mentioned.

The invention can be applied with particular advantage if the medium is a consumable oil, such as, for  
35 instance, sunflower oil, if measurement is performed at

high temperatures, or if the sensor is exposed for a relatively long time. An additional advantageous property is that the substrate has been found to adhere well to glass. As a consequence, in practice, the oxygen content  
5 can be simply determined in consumable oil products which are stored in glass, from which in turn a storage life can be derived, and the sensor will not come loose at high temperatures or in chemically aggressive environments.

In a preferred embodiment, the fluoridated silicone  
10 polymer is the polymer which is marketed by the firm of Wacker under the trademark name of Elastosil E113F. Of the tested substrate materials, this polymer has been found to exhibit the best stability at high temperature loads.

15 The invention will now be further elucidated with reference to the accompanying drawing, wherein

Fig. 1a shows a diagram schematically indicating how the sensor can be arranged in contact with the medium, with respect to a measuring unit, with the sensor arranged in  
20 the medium;

Fig. 1b shows a diagram of a combined sensor/measuring unit;

Fig. 2 shows a graph representing the resistance to photobleaching for a conventional substrate and for a  
25 substrate according to the invention;

Fig. 3 shows a graph representing the resistance to chemical action of sunflower oil for a conventional substrate and for a substrate according to the invention;

Fig. 4 shows a chart representing the resistance to  
30 temperature loading for a conventional substrate and for a substrate according to the invention.

Referring to Fig. 1a, a light transmitting container 1, for instance of glass, contains a medium 2,  
35 for instance a consumable oil. With the arrangement, the

oxygen content in oil 2 can be measured. This oxygen dissolves in the oil in that an equilibrium arises between the oxygen in the air 11 and the oxygen in the oil 2. The optical sensor 3 of the invention is arranged in the container 1 by affixing it to a wall 12. The sensor comprises a substrate 4 and an oxygen-sensitive dye 5, consisting of an organometallic complex. Light 9 of a particular wavelength spectrum, coming from a lamp 7 of a detector 6, shines on the sensor 3, thereby giving rise to fluorescence in the dye 5. The fluorescence comprises light of a different wavelength spectrum 10, which is radiated to the detector and is received on a photoelectric converter 8. According to the invention, the substrate 4 consists of a fluoridated silicone polymer. Because of the gas permeability of the substrate 4, oxygen from the oil 2 can interact with the organometallic complex. As a result, the amount of fluorescence is influenced by the amount of oxygen in the medium. By measuring the emitted intensity or life of the fluorescence 10, the extent of the influence, and hence the oxygen content, can be established.

Referring to Fig. 1b, a combined sensor/measuring unit 13 contains a lamp 7 and a photoelectric converter 8 and a sensor 3 which is arranged on the outside of the sensor/measuring unit 13. With the arrangement, for instance the gas-air ratio in combustion apparatus can be measured.

Fig. 2 shows a graph reflecting how a sensor as indicated in Fig. 1 by reference numeral 3, in two designs, was irradiated for an hour with a constant amount of light of a high light intensity. Through the effect of photobleaching, after a few minutes, a reduced fluorescence arises, as a result of which the sensor becomes less and less sensitive. In the graph, the y-axis plots a light intensity radiated by the sensor, as a consequence of the irradiation of the sensor with a constant amount of light,

normalized at 1. The x-axis plots the time, in minutes, when fluorescence was measured. It can be derived from the graph that the effect of photobleaching is considerably less for a sensor with a substrate consisting of  
5 fluoridated silicone polymer (upper line) than for a sensor with a substrate of a conventional silicone polymer (lower line). It is incidentally noted that under normal operating conditions, the light intensity used is much lower, so that the phenomena do not occur so soon. However, the deviation  
10 remains proportionally the same.

Fig. 3 represents a graph reflecting the resistance to chemical action of sunflower oil for a conventional substrate and for a substrate according to the invention; in both tests a sensor was placed in sunflower oil over a  
15 prolonged period of time of a few weeks, while the sunflower oil was exposed to air. At regular intervals the time of decay of the fluorescence was measured, i.e., the time when the intensity has decreased to  $1/e$ . Through action of the oil, for a conventional substrate, this decay  
20 time increases after some time, i.e. the sensitive substance remains fluorescent longer than in the case where no action of oil takes place, despite the fact that the oxygen concentration remains constant. The sensitivity of the sensor is therefore influenced by the action, so that  
25 no reliable measurement of the oxygen content can be made. In the graph, the y-axis plots this time of decay, normalized at 1, against the time of measurement, in days, plotted on the x-axis. It can be derived from the graph that a sensor with a substrate consisting of fluoridated  
30 silicone polymer (lower line) has a much better, substantially constant, resistance to chemical actions than does a sensor with a substrate of a conventional silicone polymer (upper line).

Fig. 4 is a chart representing the resistance to  
35 temperature loads for a conventional substrate and for a

substrate according to the invention; in both tests, a sensor was exposed to air at a high ambient temperature for five weeks. In the chart it can be seen that after exposure to this temperature a reduced fluorescence occurs, so that the sensor becomes less sensitive. In the chart, the y-axis plots a light intensity radiated by the sensor, as a result of the irradiation of the sensor with a constant amount of light, normalized at 100%. For each of three different substrate materials, the x-axis plots two respective measurements, one in which the sensor was stored at 20° C and one in which the sensor was stored at 90° C. From the chart, it can be derived that for a conventional silicone polymer (a) the intensity of the sensor decreases to 20% of the value with respect to the sensor stored at room temperature. The sensitivity of the sensor therefore decreases considerably. For a sensor with a substrate according to the invention (a mixture of PS184.5 and PS9120 of the firm United Chemicals Inc), the sensitivity decreases comparatively less, to about 30%, so that, compared with the conventional sensor, an improved temperature resistance is achieved (c). For a sensor according to the preferred embodiment, i.e., a sensor with a substrate of the type Elastosil E113F of the firm of Wacker, this temperature influence is a factor 2 less high and the intensity remains up to 70% of the value at room temperature (b).

The invention is not limited in any way to the exemplary embodiments described and represented here, but encompasses all kinds of modifications, naturally insofar as they fall within the scope of protection of the claims following below.

## CLAIMS

1. An optical sensor for measuring oxygen in a medium, provided with a substrate in which an organometallic complex is embedded, characterized in that the substrate consists of a fluoridated silicone polymer.
- 5 2. An optical sensor according to claim 1, characterized in that the silicone polymer is the polymer which is marketed by the firm of Wacker under the trademark name Elastosil E113F.

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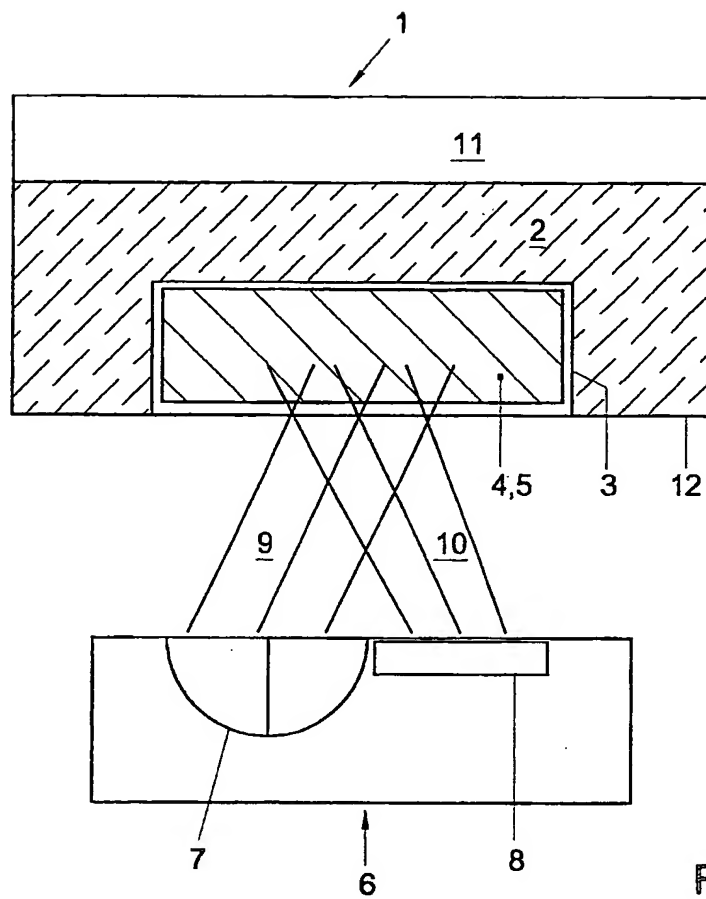


Fig. 1a

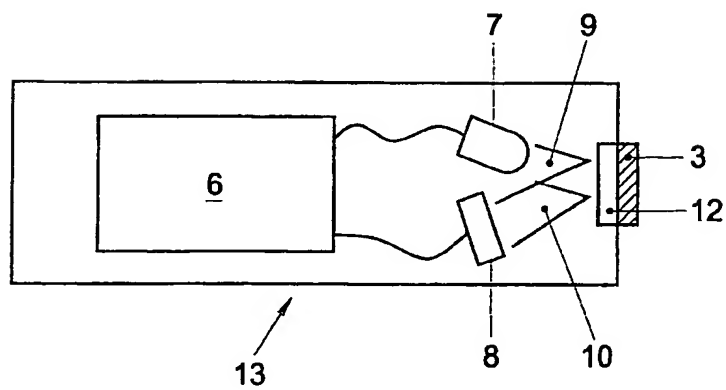


Fig. 1b

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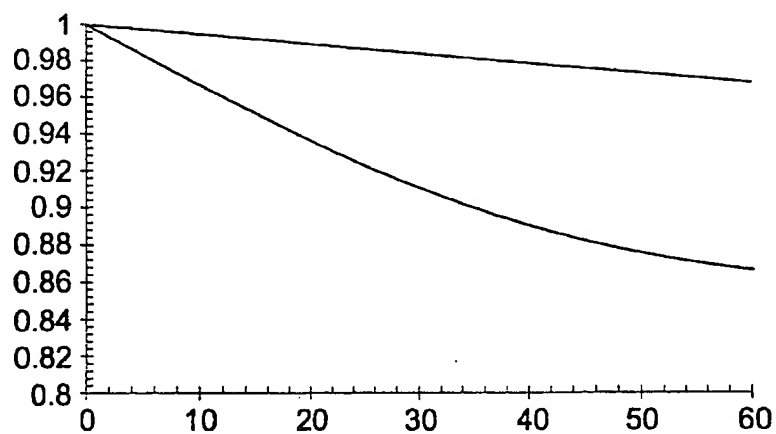


Fig. 2

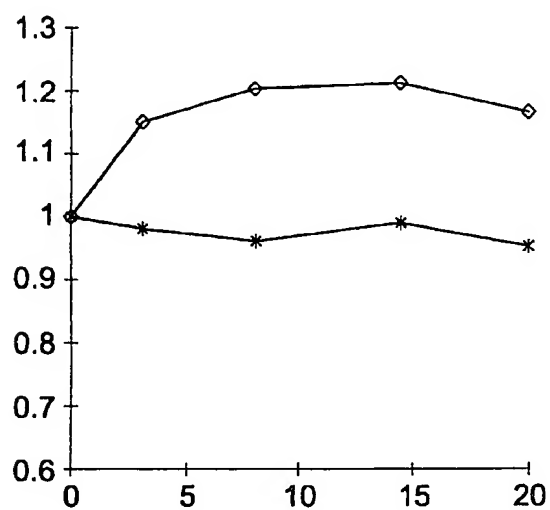


Fig. 3

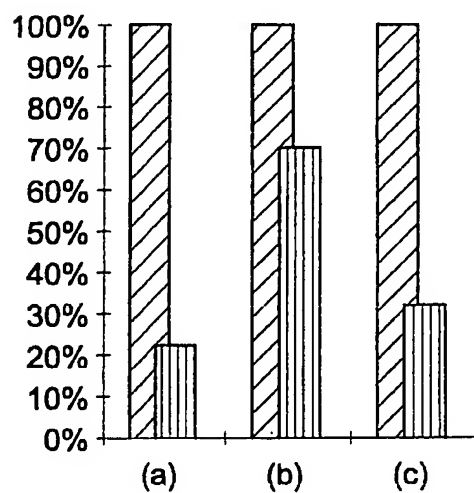


Fig. 4

# INTERNATIONAL SEARCH REPORT

Int. .onal Application No

PCT/NL 01/00150

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 G01N21/77 G01N21/64 G01N31/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 656 241 A (SEIFERT KEVIN R ET AL) 12 August 1997 (1997-08-12) column 13, line 20 - line 40 column 14, line 50 - line 53 ---	1
A	US 5 965 642 A (CARLSON W BRENDEN ET AL) 12 October 1999 (1999-10-12) column 4, line 18 - line 31 column 7, line 4 - line 20 ---	1
A	GB 2 132 348 A (UNIV VIRGINIA) 4 July 1984 (1984-07-04) page 3, line 74 - line 109 -----	1

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Verdoodt, E

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. .onal Application No

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